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Influence of V/III molar ratio on the formation of In vacancies in InN grown by metal-organic vapor-phase epitaxy

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We have applied a slow positron beam to study InN samples grown by metal-organic vapor-phase epitaxy with different V/III molar ratios (3300–24 000) and at different growth temperatures (550–625 °C). Indium vacancies were identified in samples grown at V/III ratios below 4000. Their concentration is in the 10^{17}cm^{-3} range. No strong dependence of vacancy concentration on the molar ratio was observed. At low V/III ratios, however, In droplets and vacancy clusters are formed near the substrate interface. The elevated growth temperature enhances the In vacancy formation, possibly due to limited sticking of In on the growth surface close to the decomposition temperature. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2219335]

Indium nitride is a promising material for, e.g., high electron mobility transistors (HEMTs), light-emitting diodes, and lasers.[1,2] Much of the recent research on this material has concentrated on the magnitude of the band gap. The possible narrow band gap of InN [~0.7 eV Ref. 3 and 4] allows the III-N ternary alloy systems to extend the spectral range from infrared to deep ultraviolet, which is advantageous, e.g., for multijunction solar cell technology.[3]

The growth of high quality InN is rather difficult. Bulk material is not available but high quality films on sapphire have been fabricated by molecular beam epitaxy[5,6] (MBE) and also by metal-organic vapor-phase epitaxy (MOVPE).[7,8] The properties of the material are greatly affected by the layer thickness and substrate material[9,10] as well as the growth temperature and the stoichiometry.

In this work we utilize positron annihilation spectroscopy to study the effect of different stoichiometry conditions, i.e., V/III molar ratio and growth temperature, on vacancy formation in InN grown by MOVPE. Indium vacancies and vacancy clusters have been identified in previous positron studies on MBE-InN.[9] In addition, the vacancy concentration has been observed to correlate with the free electron density and to anticorrelate with the electron mobility.[11]

We use a low-energy positron beam and two Ge detectors to measure the Doppler broadening of the positron-electron annihilation radiation. The electron momentum density is described by the conventional low momentum parameter S and the high momentum parameter W. The reduced electron density at vacancies increases the S parameter and decreases the W parameter. Annihilations of trapped positrons with core electrons (W parameter) give information on the atoms surrounding the vacancy.

Eight samples were grown by MOVPE in Université Montpellier II Ref. 7 (Table I). The thicknesses of the InN layers grown directly on sapphire substrate varied from 200 to 1400 nm. The V/III molar ratios used during the growth process were between 3300 and 24 000. Growth temperatures were in the range of 550–625 °C. Samples 7 and 8, grown at the most In-rich conditions, have visible droplets at the surface. These droplets have been identified as metallic indium. A MBE-InN sample was measured as a reference. This sample has no positron trapping vacancy defects according to previous positron lifetime and Doppler broadening studies.[9,11]

The samples were measured with positron implantation energies from 0.5 to 38 keV (depth scan). The S parameter at the sample surface ($E<2$ keV) is high, reflecting the low electron density at the surface (Fig. 1). The plateau starting at energies of 2 keV corresponds to the InN layer. At higher energies the S parameter decreases as the positrons start to reach the substrate. The MBE grown InN reference layer has the lowest S parameter, which is the value related to positron annihilation in the InN lattice.[9] In the MOVPE samples the S parameter is clearly higher than in the MBE reference. However, there is no obvious correlation with the V/III ratio. This indicates that vacancies are observed in MOVPE-InN, but the V/III molar ratio does not have a clear role in the vacancy defect formation in the range of 5000–24 000.

The S parameter depth scans for three samples with lowest V/III molar ratios are presented in Fig. 2. The curves measured in samples 7 and 8 have a local minimum at depths

TABLE I. Growth parameters of the measured samples and the vacancy concentrations estimated from the results of positron annihilation measurements.

Sample No.	V/III molar ratio	Thickness (μm)	Growth temperature (°C)	Vacancy concentration (cm^{-3})
1	24 000	0.2	550	9×10^{16}
2	15 000	<0.3	550	7×10^{16}
3	10 000	0.3	550	2×10^{17}
4	4 840	0.6	550	9×10^{16}
5	4 840	0.5	625	4×10^{17}
6	4 840	0.6	600	7×10^{17}
7	3 650	1.4	550	8×10^{16}
8	3 267	0.9	550	1×10^{17}

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[b]Deceased.

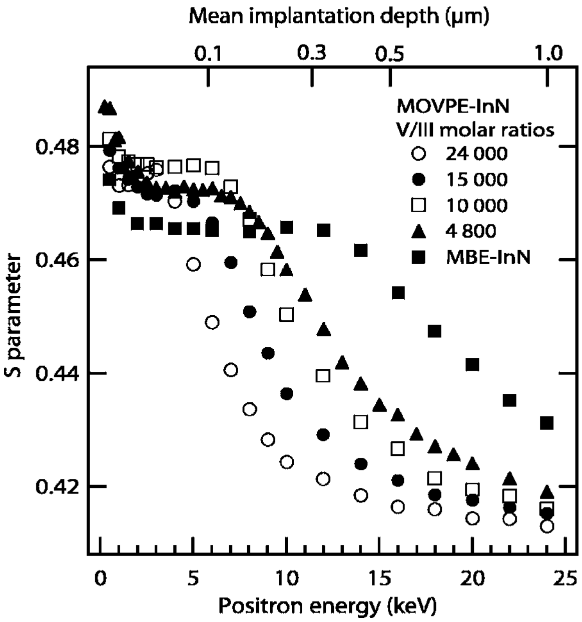

FIG. 1. The S parameters as a function of positron implantation energy measured in samples grown with V/III molar ratios larger than 4000.

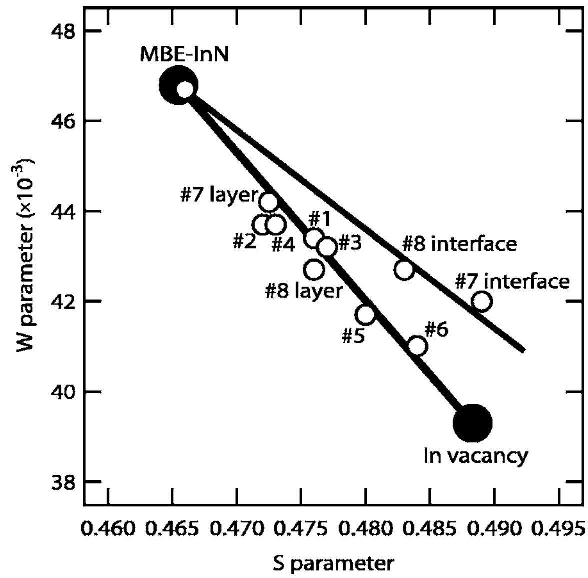

FIG. 3. The W parameter as a function of the S parameter. The linearity between the layer specific parameters indicates that the same kind of vacancy (In vacancy) is present in all the layers. The S parameters for vacancy clusters, formed close to the interface, form a line with a gentler slope and are thus distinguishable from the In vacancies.

of 50 nm. When the positron implantation energy is increased the S parameters rise and form maxima when the mean positron implantation depth is close to 0.4 μm. This indicates that the vacancy defect profile in the InN films is inhomogeneous, with clearly higher vacancy concentrations closer to the InN/sapphire interface.

The W vs S parameter plot for the InN layers is presented in Fig. 3. The (S,W) parameters have been chosen at positron implantation energies where annihilations at the InN layers are maximized. Due to the nonconstant S vs E curves in samples 7 and 8, we chose two parameters: (i) one measured closer to the surface corresponding to a lower S parameter (marked in Fig. 3 with "layer") and (ii) the other one

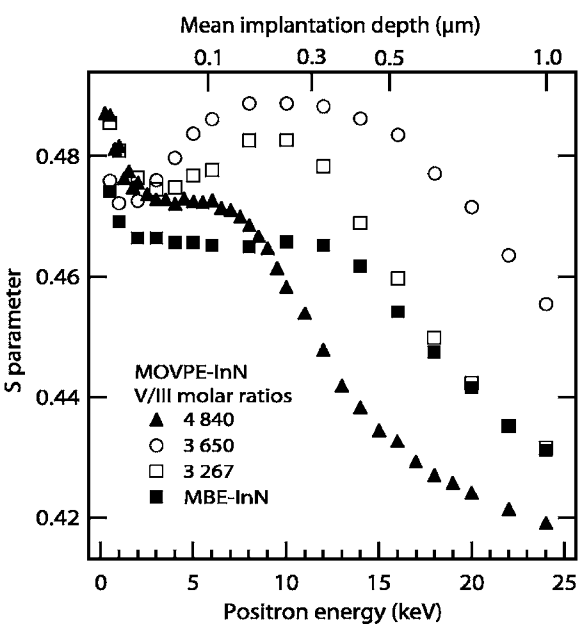

FIG. 2. The S parameters in samples grown with V/III molar ratios below 5000. The S parameter increases at higher positron implantation energies which indicates that the vacancy concentration increases towards the interface.

close to the InN-substrate interface, where S is much larger ("interface" in Fig. 3).

The layer (S,W) values fall on the same line in all samples including the MBE grown reference sample. This indicates that positrons annihilate in two states, as free positrons in the bulk and as trapped positrons at vacancies. Additionally, it can be concluded that the observed vacancy is the same for all these samples. The slope of this line is the same as determined for the In vacancy.[9] This indicates that In vacancies are formed in MOVPE growth, similarly as observed in the case of MBE-InN.

The two interface (S,W) values determined in samples 7 and 8 form a line with the MBE-InN values with a different slope. Previous studies on GaN samples show that this is typical behavior of the (S,W) plot when vacancy clusters are present.[12] Indium droplets were observed at the surfaces of these two samples. The indium droplet formation can thus be considered to be accompanied by the formation of vacancy clusters. InN grown with low V/III ratio seems to be similar to GaN, where vacancy clusters have been observed in Ga-rich conditions in N-polar growth using MBE.[12] Cluster formation may indicate that also N sites are left empty at very low V/III molar ratios.

The vacancy concentrations in the samples can be estimated using the standard positron trapping model [Eq. (1)], with the layer specific S parameters

$$c_V = \frac{N_{\mathrm{at}}}{\mu_V \tau_b} \frac{(S/S_b - 1)}{(S_V/S_b - S/S_b)}, \tag{1}$$

where $S_V = 1.046 S_b$ (Ref. 9 and 11) is the S parameter specific to the In vacancy, $\mu_V = 2 \times 10^{15}\ \mathrm{s}^{-1}$ (see Ref. 13) is the positron trapping coefficient, $N_{\mathrm{at}} = 6.367 \times 10^{22}\ \mathrm{cm}^{-3}$ is the atomic density, and $\tau_b = 184$ ps is the positron lifetime in vacancy-free InN.[9] The S parameter of the MBE grown sample was taken for S_b (0.4655), characterizing the InN lattice.

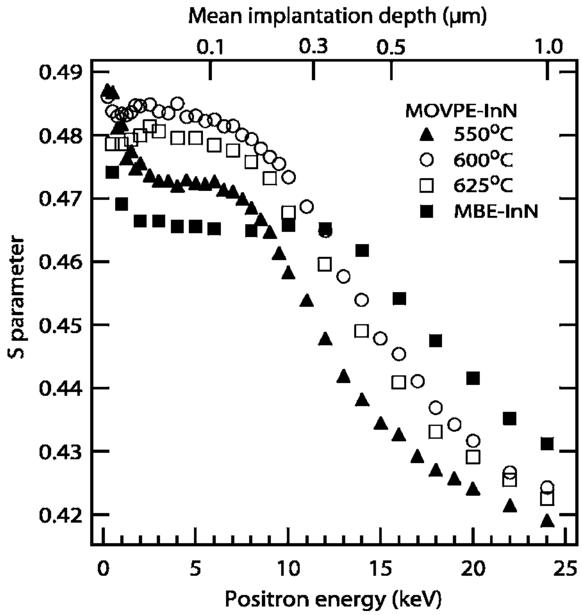

FIG. 4. The S parameter as a function of positron implantation energy in InN samples grown at different temperatures. The layer specific S parameter increases when the growth temperature is raised.

The In vacancy concentrations vary from high $10^{16}\mathrm{cm}^{-3}$ to low 10^{17} cm^{-3} in all samples grown at 550 °C. Interestingly, these densities are very similar to those detected in MBE samples of the same thicknesses (200–300 nm).[9,11] This suggests that In vacancy formation is dominated by thickness-dependent properties, such as strain or dislocation density, and that it is less dependent on growth thermodynamics or stoichiometry. In fact, the calculated formation energies of In vacancies are high,[14] which is in agreement with the positron result showing their absence in thick ($\sim$1 μm) MBE layers.[9,11]

The effect of growth temperature on the formation of vacancy defects was studied by comparing samples 4–6. The results in Fig. 4 show that the S parameter of the InN layer increases with growth temperature. The points in (S,W) plot fall on the line corresponding to V_{In} (Fig. 3) indicating that In vacancy remains as the dominant defect. More In lattice sites are thus left empty when the growth takes place close to the decomposition temperature of InN, perhaps because of the limited sticking of indium on the growth surface.

In summary, positron annihilation measurements were performed in MOVPE-InN. Vacancy defects were observed at concentrations of $\sim 10^{17}$ cm^{-3} and identified as indium vacancies. In vacancy concentration is almost independent of the V/III molar ratio at 4800–24 000. At lower ratios, below 4000, the In droplet formation is accompanied by the formation of vacancy clusters. The In vacancy formation depends on the growth temperature. The concentration was observed to increase from 10^{17} to 10^{18} cm^{-3} when the growth temperature was increased from 550 °C close to the decomposition temperature of 625 °C.

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